Density functional theory modeling of chemical reactions at interfaces

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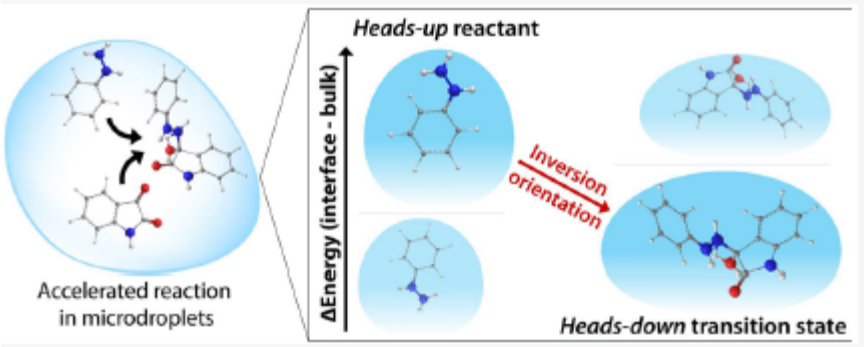
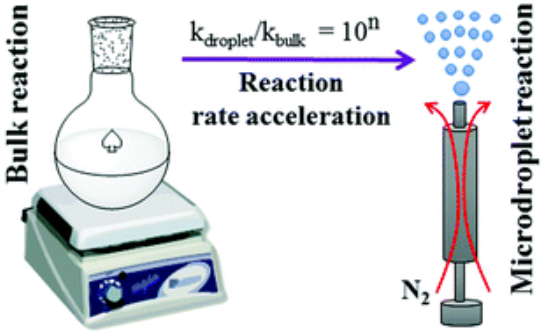
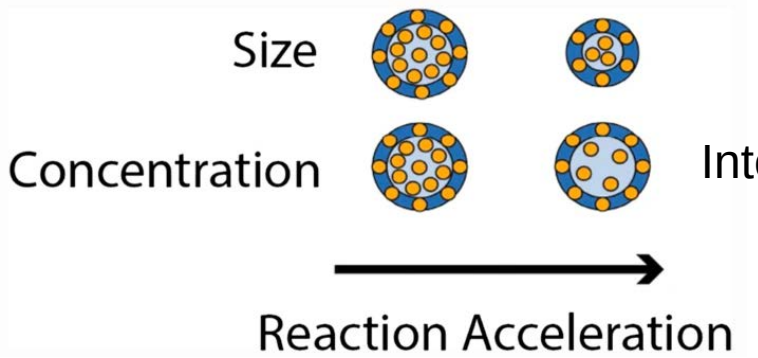


Motivation

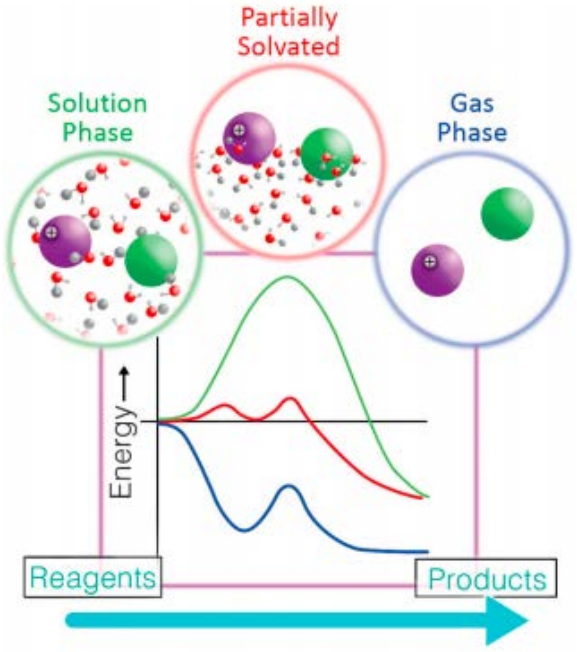
Reaction acceleration observed for organic reactions in microdroplets





Interface effects at droplet surface cause acceleration

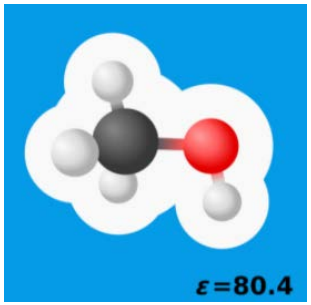
Hypothesis:
Partially solvated species at interface reduce activation energy of reaction



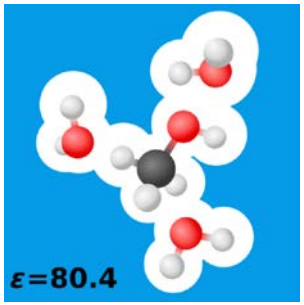
Yan, Xin et al *Angewandte Chemie International Edition* 55.42 (2016): 12960-12972.
Marsh, Brett M. et al *Journal of The American Society for Mass Spectrometry* 30.10 (2019): 2022-2030.
Banerjee, Shibdas, et al *Analyst* 142.9 (2017): 1399-1402.

DFT for solvents

Chemical reactions usually modeled with continuum solvation models

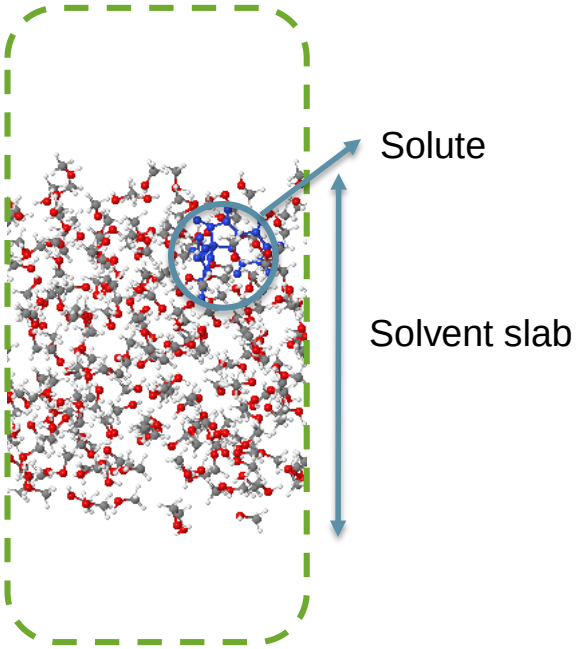


Implicit model



Mixed model

Does not work for interface



Explicit model

Explicit solvent for air/liquid interface modeling:

- 2.5 nm solvent slab needed (~1400 atoms)
- Statistical nature of solvent molecules – need to sample large configuration phase
- Self-consistent Density Functional Tight Binding (DFTB) used

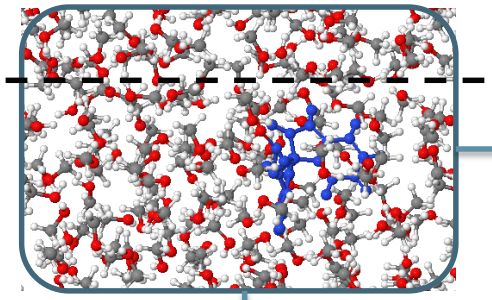
Basdogan, Yasemin, et al *Wiley Interdisciplinary Reviews: Computational Molecular Science* 10.2 (2020): e1446.

DFTB simulation workflow

100 runs

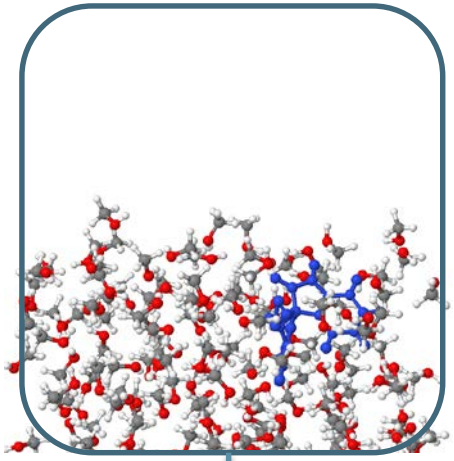
Packmol-Random Bulk configuration

DFTB relax



Energy of solute in bulk

Slice bulk in XY plane & add vacuum – creates interface structure



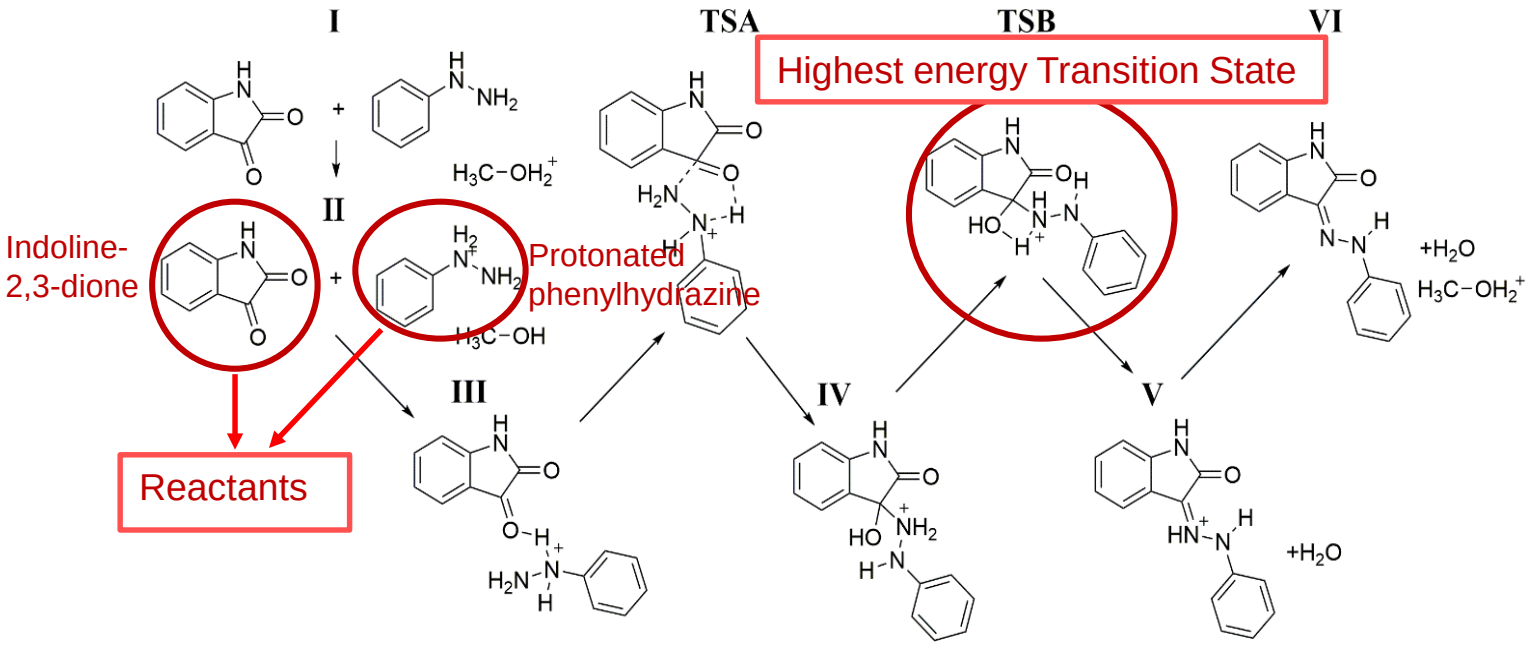
Energy of solute at interface

Correlation between bulk & interface configuration :

- ✓ Can tell us impact of only the interface on energy
- ✓ Reduce number of solvent configurations needed

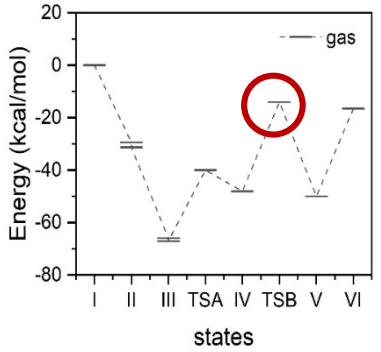
Hydrazone reaction pathway

Gaussian B3LYP used to find reaction pathway in gas phase



Reaction rate $R \propto e^{-E_a/k_B T}$

Activation energy, $E_A = E_{Transition\ State} - \sum E_{Reactants}$

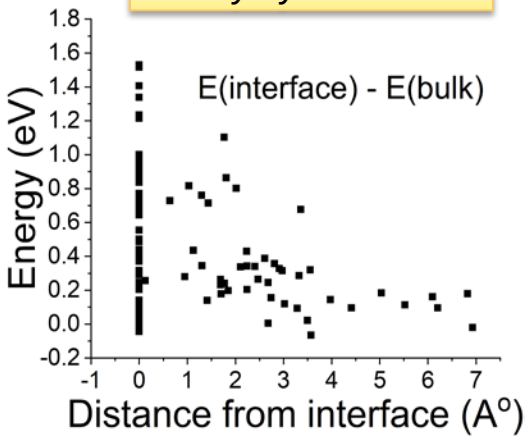


Energy of reaction pathway

Energetics at interface

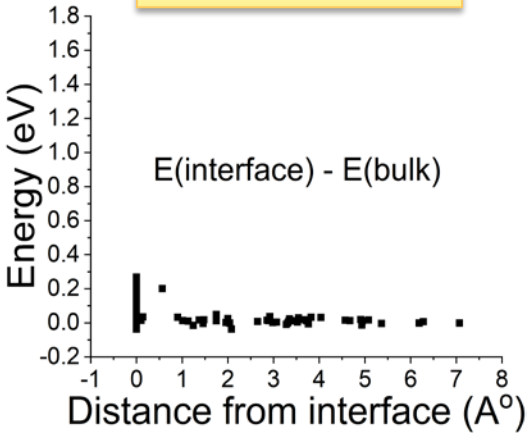
Explicit solvent DFTB calculations for hydrazone formation in methanol

Phenylhydrazine-H+



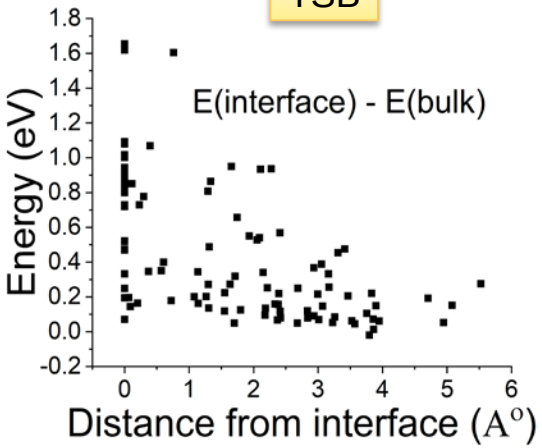
Charged reactant

Indoline-2,3-dione



Neutral reactant

TSB



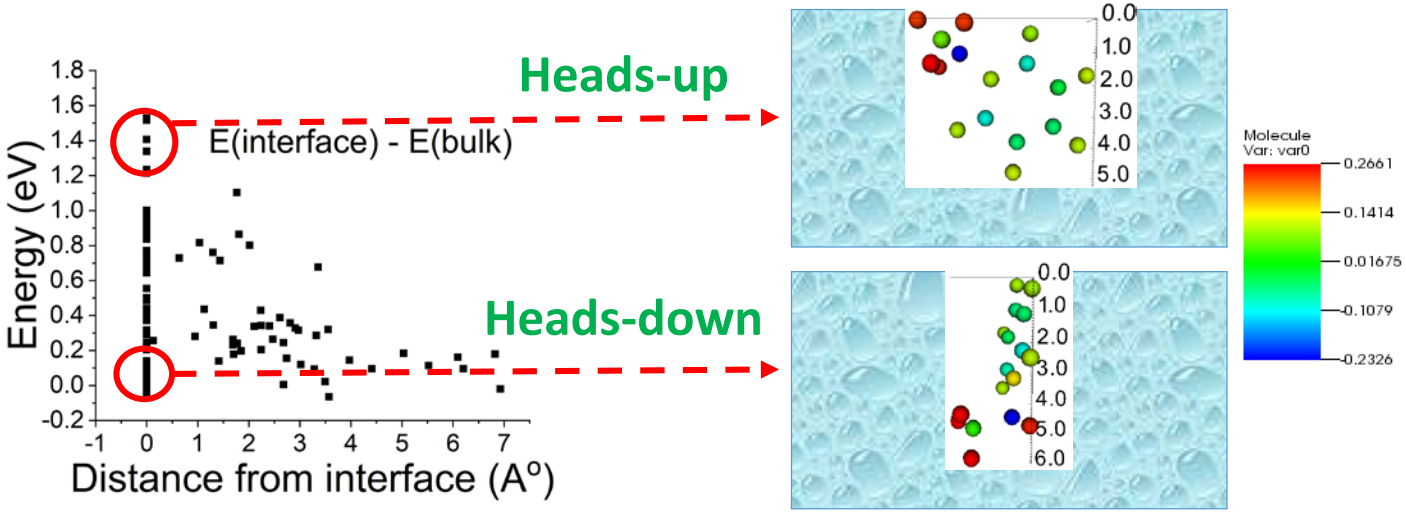
Charged TS

- ❑ Charged molecules - Large solvation effect at interface
- ❑ Neutral molecules – Energy difference much lower between bulk/interface

Narendra, Namita, et al *The Journal of Physical Chemistry A* 124.24 (2020): 4984-4989.

Charge analysis

Charge distribution for phenylhydrazine-H+



Charged molecule

- ❑ Heads-up : High energy configuration; Least solvated
- ❑ Heads-down : Low energy configuration; Fully solvated

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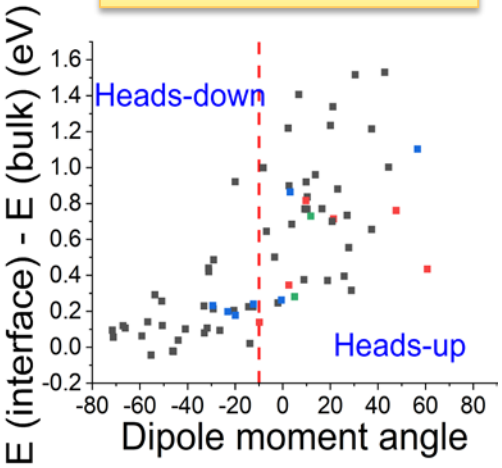
Charge analysis

Phenylhydrazine-H+



Charged reactant

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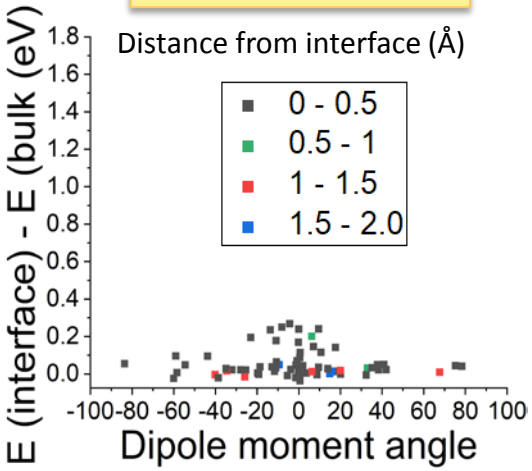
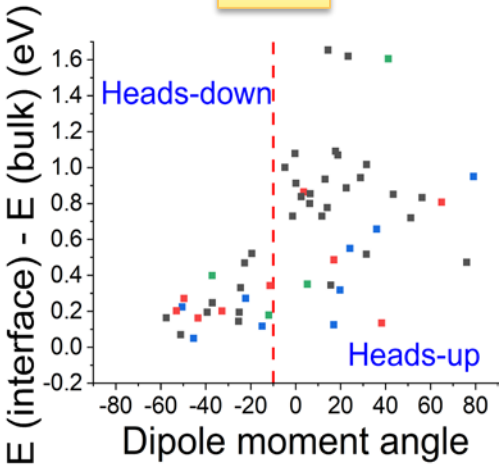


Neutral reactant

TSB

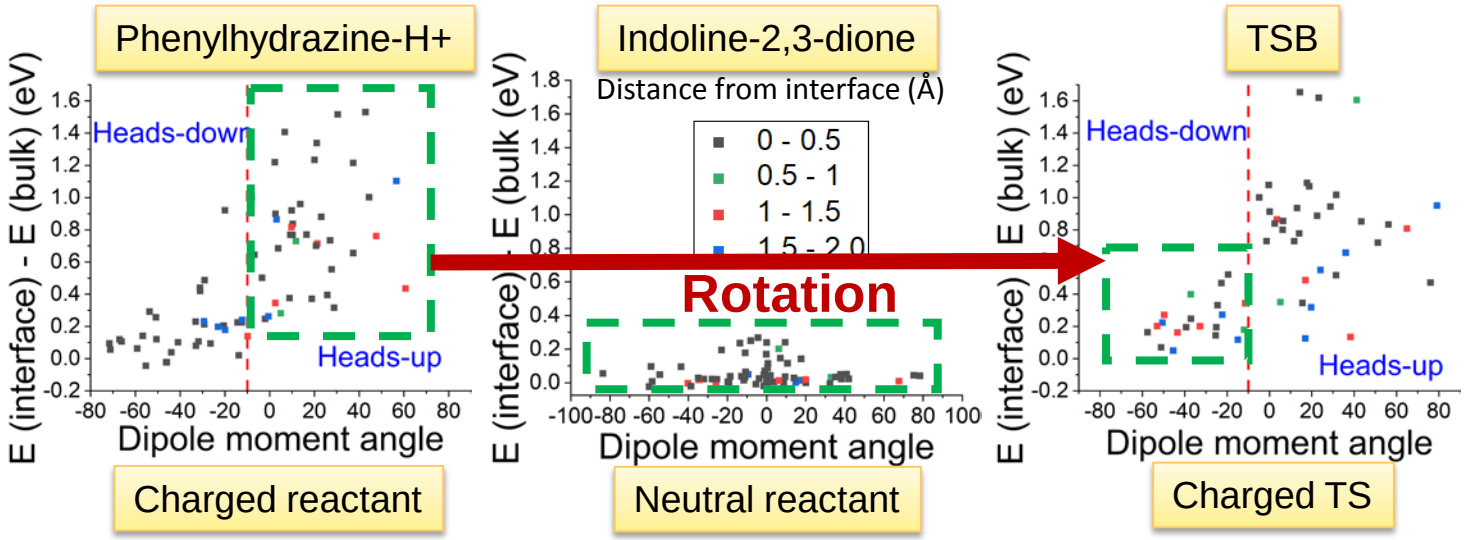


Charged TS

- Charged molecule
  Correlation of high energy/positive dipole vs low energy/negative dipole
- Neutral molecule
  No dipole dependence

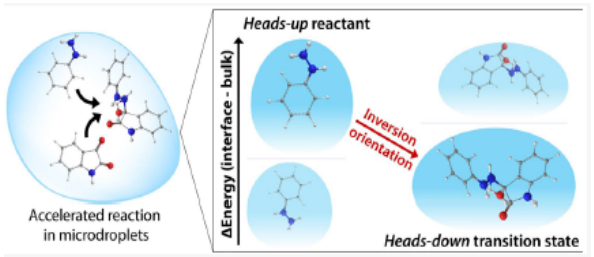
Narendra, Namita, et al *The Journal of Physical Chemistry A* 124.24 (2020): 4984-4989.

Reaction rate acceleration



Heads-up phenylhydrazine → Heads-down TSB:

- ❑ Highest reaction rate pathway
- ❑ 612 meV decrease in activation energy from bulk to interface
- ❑ Probability of heads-up phenylhydrazine ~ 10^{-6} (calculated from partition function)



Predicted acceleration factor of 10^4 matches experimental value

Narendra, Namita, et al *The Journal of Physical Chemistry A* 124.24 (2020): 4984-4989.

Summary

- DFT based methodology verified to model reactions at droplet surface
- Reaction pathway involving partially solvated reactant at the microdroplet surface causes reaction acceleration
- Extended study to more organic reactions (benzimidazole, purine, adenine, benzoxazole). Observed interface solvation effects hold.